(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 September 2002 (26.09.2002)

PCT

(10) International Publication Number
WO 02/074430 A1

(51) International Patent Classification[7]: B01J 13/18, C11D 3/50, A61K 7/00

(21) International Application Number: PCT/GB02/01133

(22) International Filing Date: 13 March 2002 (13.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0106560.6 16 March 2001 (16.03.2001) GB

(71) Applicant *(for all designated States except US)*: **QUEST INTERNATIONAL B.V.** [NL/NL]; Huizerstraatweg 28, NL-1411 GP Naarden (NL).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **NESS, Jeremy, Nicholas** [GB/GB]; 25 High Snoad Wood, Challock, Ashford, Kent TN25 4DQ (GB).

(74) Agent: **KEITH W. NASH & CO.**; 90-92 Regent Street, Cambridge CB2 1DP (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/074430 A1

(54) Title: PERFUME ENCAPSULATES

(57) Abstract: A perfume encapsulate comprises an aminoplast capsule, the capsule shell comprising urea-formaldehyde or melamine-formaldehyde polymer and a second polymer comprising a polymer or copolymer of one or more anhydrides, preferably ethylene/maleic anhydride copolymer. The second polymer improves the stability of the capsules with respect to surfactant, thus improving perfume retention properties and enabling use of the capsules in aqueous surfactant-containing products in a way that has not hitherto been possible.

Title: Perfume Encapsulates

Field of the Invention

This invention concerns perfume encapsulates, and relates to perfume encapsulates, a method of making the encapsulates and aqueous products including the encapsulates.

Background to the Invention

It is known to encapsulate perfume in small capsules (or micro-capsules), typically having a diameter less than 1000 microns, for a variety of reasons relating to the protection, delivery and release of perfume. One type of capsule, referred to as a wall or shell capsule, comprises a generally spherical hollow shell of perfume-insoluble material, typically polymer material, within which perfume is contained.

Various methods are known for making shell capsules, including in situ polycondensation for producing so-called aminoplast resin capsules from urea-formaldehyde or melamine-formaldehyde polymers. Briefly, the process involves forming a dispersion or emulsion of the perfume in an aqueous solution of urea-formaldehyde or melamine-formaldehyde precondensate under appropriate conditions of agitation to produce capsules of a desired size, and adjusting the reaction conditions to cause condensation of the precondensate by acid catalysis, resulting in the condensate separating from solution and surrounding the dispersed perfume fill to produce micro-capsules.

Perfume-containing aminoplast capsules are currently primarily used in the area of perfume sampling as so-called "scratch and sniff" products, where the capsules are applied to paper or cardboard and show excellent perfume retention properties over extended periods, with the capsule functioning to prevent evaporation of the perfume until the capsules is ruptured. Such capsules can similarly be applied to textiles etc, and also show good stability.

It has been proposed to use such capsules in shampoo and other aqueous surfactant-containing products to give various fragrance effects, e.g. burst release in-use, enhanced deposition, longevity, stability improvement etc. However, in practice serious storage problems arise with shell encapsulates in such products, in that surfactant is able to enter the capsule through the wall and causes the perfume contents to leach out. Aminoplast capsules are most resistant to this effect, but nevertheless still exhibit quite rapid perfume loss such that they are of no practical use in such products. In this connection, see the article "Use of amino resin microcapsule dispersions in cosmetics" in Parfumerie und Kosmetik, 72 Jahrgang, Nr. 7/91.

The present invention is concerned with modified aminoplast capsules having properties enabling use in aqueous surfactant-containing products.

Summary of the Invention

In one aspect the present invention provides a perfume encapsulate comprising an aminoplast capsule, the capsule shell comprising urea-formaldehyde or melamine-formaldehyde polymer and a second polymer comprising a polymer or copolymer of one or more anhydrides.

The second polymer preferably comprises a polymer or copolymer of one or more cyclic anhydrides, preferably maleic anhydride. It is particularly preferred that the second polymer comprises ethylene/maleic anhydride copolymer.

The aminoplast capsule preferably comprises melamine-formaldehyde polymer resin.

The aminoplast capsule may be made in generally conventional manner, e.g. as described in GB 2073132-A and WO 98/28396 (see Examples 15 and 16).

In a further aspect, the invention provides a method of making a perfume encapsulate, comprising forming a dispersion of perfume in an aqueous solution of urea-formaldehyde or

melamine-formaldehyde precondensate and a second polymer comprising a polymer or copolymer of one or more anhydrides; and causing polymerisation of the precondensate to produce perfume-containing aminoplast capsules.

The dispersion is suitably agitated or stirred, with polymerisation occurring by acid-catalysed condensation reaction.

The resulting capsules may be separated, e.g. by filtering.

It is found that the presence of the second polymer improves the stability of the capsules relative to surfactant, thus improving perfume retention properties. The mechanism by which the second polymer improves the stability of the capsules is not fully understood, but it can be speculated that the second polymer is incorporated into the urea-formaldehyde or melamine-formaldehyde polymer structure in such a way that it can stiffen the capsule walls and prevent formation of any porosity that would allow the ingress of surfactant to the capsule interior.

GB 2073132-A refers on page 2 line 52 to the possible use of ethylene/maleic anhydride copolymer, although this is stated not to be within the scope of the invention of that specification. The previous line of the specification refers to polyvinyl alcohol in similar terms, although as will be apparent from the Example below polyvinyl alcohol does not function to improve capsule stability in the same way as the second polymer of the present invention. Furthermore, that specification does not concern perfume encapsulates but relates particularly to capsules for use in pressure-sensitive copying systems. GB 2703132-A is concerned with stabilising the liquid fill/precondensate dispersion, and makes no reference to the stability properties of the resulting capsules.

The term "perfume" is used in this specification to mean any odoriferous material generally (but not necessarily) having an odour that is considered pleasant or attractive, or any material which acts as a malodour counteractant.

As is well known, a perfume normally consists of a mixture of a number of perfumery materials, each of which has an odour or fragrance. The number of perfumery materials in a perfume is typically 10 or more. The range of fragrant materials used in perfumery is very wide; the materials come from a variety of chemical classes, but in general are water-insoluble oils. In many instances, the molecular weight of a perfumery material is in excess of 150, but does not exceed 300.

The perfumes used in the present invention can be mixtures of conventional perfumery materials. Such materials are, for example, natural products such as extracts, essential oils, absolutes, resinoids, resins, concretes etc., but also synthetic materials such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, nitriles, etc., including saturated and unsaturated compounds, aliphatic, carbocyclic, and heterocyclic compounds.

Such perfume materials are mentioned, for example, in S. Arctander, Perfume and Flavor Chemicals (Montclair, N.J., 1969), in S. Arctander, Perfume and Flavor Materials of Natural Origin (Elizabeth, N.J., 1960) and in "Flavor and Fragrance Materials – 1991", Allured Publishing Co. Wheaton, Ill. USA.

Examples of perfume materials which can be used in the invention are: geraniol, geranyl acetate, linalol, linalyl acetate, tetrahydrolinalol, citronellol, citronellyl acetate, dihydromyrcenol, dihydromyrcenyl acetate, tetrahydromyrcenol, terpineol, terpinyl acetate, nonpol, nopyl acetate, 2-phenyl-ethanol, 2-penylethyl acetate, benzyl alcohol, benzyl acetate, benzyl salicylate, styrallyl acetate, benzyl benzoate, amyl salicylate, dimethylbenzyl-carbinol, trichloromethylphenyl-carbinyl acetate, p-tert-butylcyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, α-hexylcinnamaldehyde, 2-methyl-3-(p-tert-butylpheyl)propanal, 2-methyl-3-(p-isopropylphenyl)propanal, 2-(p-tert-butylpheyl)-propanal, 2,4-dimethyl-cyclohex-3-enyl-carboxaldehyde, tricyclodecenyl acetate, tricyclodecenyl propionate,4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarboxyaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexenecarboxaldehyde, 4-acetoxy-3-pentyl-tetrahydropyran, 3-carboxymethyl-2-pentylcyclopentane, 2-n-heptylcyclopentanone, 3-methyl-2-pentyl-2-cyclopentenone, n-decanal, n-dodecanal, 9-decenol-1, phenoxyethyl isobutyrate, phenyl-acetaldehyde dimethyl-acetal, phenylacetaldehyde diethylacetal, geranyl nitrile, citronellyl

nitrile, cedryl acetate, 3-isocamphylcyclohexanol, cedryl methyl ether, isolongifolanone, aubepine nitrile, aubepine, heliotropin, coumarin, eugenol, vanillin, diphenyl oxide, hydroxycitronellal, ionones, methylionones, isomethylionones, irones, cis-3-hexenol and esters thereof, indan musks, tetralin musks, isochroman musks, macrocyclic ketones, macrolactone musks, ethylene brassylate.

The perfume should be substantially free of water-miscible materials such as dipropylene glycol. Solvents which can be used for perfumes include, for example: diethyl phthalate, triethyl citrate, isopropyl myristate, etc.

The perfume may optionally include one or more adjuncts. For example, the perfume may include one or more release modifiers, which change the evaporation profile of the perfume after the capsule has been broken; these are essentially fixatives such as non-volatile oils. The perfume may additionally or alternatively include one or more stiffening agents, which function to make the capsule less easy to break, for example by being solid at room temperature. Such an agent could also function as a release agent, e.g. stearyl alcohol. The perfume may additionally or alternatively include other functional additives such as sun-screen agents etc.

The capsules typically have a diameter in the range 1 to 500 microns, preferably 5 to 300 microns, more preferably 10 to 50 microns, with the wall typically having a thickness in the range 0.1 to 50 microns. By modifying process conditions capsules of a desired size can be produced in known manner. If necessary, the capsules as initially produced may be filtered or screened to produce a product of greater size uniformity.

Capsules wall thickness may be regulated and controlled in conventional manner, by varying the relative proportions of perfume and polymer.

The capsule wall or contents may include optional dyes and/or pigments.

The improved stability of the capsules in surfactant resulting from the presence of the second polymer means that the capsules can be used in a range of surfactant-containing water-based

products in a way that has not hitherto been possible. Such products include a wide range of consumer products including shampoos and hair conditioners, shower gels and body washes, laundry detergent liquids, fabric rinse conditioners, household cleaners and bleaches, toilet cleaners and bleaches etc. The capsules may also be used in solid products such as bar toilet soap (which typically has about 10% by weight water content).

The invention thus also includes within its scope an aqueous surfactant-containing product (such as those mentioned above) comprising perfume encapsulates in accordance with the invention.

The product may otherwise by of generally conventional composition, as is known to those skilled in the art.

The perfume encapsulates may be incorporated in the product in appropriate amount to achieve desired fragrance effects.

The invention will be further described, by way of illustration, in the following example.

Example

This example illustrates the improved stability of the capsules of the invention compared to conventional capsules.

The following perfume was prepared:

Perfume A (all figures % by weight)

Allyl amyl glycollate	3.0
Citral diethyl acetal	5.3
Linalool	32.0
Linalyl acetate	30.2
Litsea cubeba oil	3.0

Orange oil Brazilian	26.5

Capsules of the following composition were produced using the method of Example 15 of WO98/28396:

Ingredient (weight in g)	Capsule A	Capsule B	Capsule C
Trimethylolmelamine condensate*	5.0	2.5	3.0
Polyvinyl alcohol**	-	2.5	-
Ethylene/maleic anhydride copolymer	-	-	2.0
Perfume A	60.0	60.0	60.0

* Beetle resin PT336 ex British Industrial Plastics Ltd

** Gohsenol GH-23 ex Nippon Gohsei

By controlling the stirring and other reaction conditions, all three capsule samples were adjusted to approximately the same mean size of 25μm.

A hair shampoo was prepared with the following base formulation:

Ingredient	% by weight
Sodium lauryl ether (2 mole) sulphate	9.6
Ammonium lauryl ether (2 mole) sulphate	4.5
Sodium chloride	2.0
Citric acid	q.s. to give pH 6.0-6.5
Preservative	q.s.
Water	balance to 100%

Capsules A, B and C were incorporated into the shampoo at a level equivalent to a perfume dosage of 0.2wt%. These samples were stored in glass jars at 37°C for one month and samples examined with a transmission light microscope.

Capsules A (aminoplast reference) had lost substantially all of their fragrance contents.
Capsules B (modified aminoplast with polyvinyl alcohol) had lost substantially all of their fragrance contents.
Capsules C (capsules of the invention) had retained the bulk of their fragrance contents.

This example thus illustrates the efficacy of the capsules of the invention in terms of perfume retention properties when incorporated in a surfactant-containing product.

Claims

1. A perfume encapsulate comprising an aminoplast capsule, the capsule shell comprising urea-formaldehyde or melamine-formaldehyde polymer and a second polymer comprising a polymer or copolymer of one or more anhydrides.

2. An encapsulate according to claim 1, wherein the second polymer preferably comprises a polymer or copolymer of one or more cyclic anhydrides.

3. An encapsulate according to claim 2, wherein the second polymer comprises maleic anhydride.

4. An encapsulate according to claim 3, wherein the second polymer comprises ethylene/maleic anhydride copolymer.

5. An encapsulate according to any one of the preceding claims, wherein the shell comprises melamine-formaldehyde polymer.

6. A method of making a perfume encapsulate, comprising forming a dispersion of perfume in an aqueous solution of urea-formaldehyde or melamine-formaldehyde precondensate and a second polymer comprising a polymer or copolymer of one or more anhydrides; and causing polymerisation of the precondensate to produce perfume-containing aminoplast capsules.

7. An aqueous surfactant-containing product comprising perfume encapsulates in accordance with any one of claims 1 to 5.

8. A product according to claim 7, selected from shampoos and hair conditioners, shower gels and body washes, laundry detergent liquids, fabric rinse conditioners, household cleaners and bleaches, toilet cleaners and bleaches, and bar toilet soap.

INTERNATIONAL SEARCH REPORT

I... tional Application No
PCT/GB 02/01133

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J13/18 C11D3/50 A61K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 251 386 A (SAEKI KEISO ET AL) 17 February 1981 (1981-02-17) column 3, line 65 -column 4, line 6; claims 1,3,10 ---	1-6
X	US 4 100 103 A (FORIS PETER L ET AL) 11 July 1978 (1978-07-11) column 5, line 32 -column 5, line 32; claims 1,9,14 ---	1-6
X	EP 0 364 922 A (MITSUBISHI PAPER MILLS LTD) 25 April 1990 (1990-04-25) page 4, line 52 -page 4, line 53; claims 7-12 --- -/--	1-3,5,6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 June 2002	02/07/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Willsher, C

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/01133

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 043 161 A (SOPER JON C ET AL) 27 August 1991 (1991-08-27)	1-3,5
A	column 2, line 45 -column 2, line 56; claims 1,5,9,11; example 3	4,6-8

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 02/01133

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4251386 A	17-02-1981	JP 54025277 A	26-02-1979
		DE 2832637 A1	08-02-1979
		ES 472115 A1	01-10-1979
		GB 2001927 A ,B	14-02-1979
		US 4356109 A	26-10-1982
US 4100103 A	11-07-1978	AR 218281 A1	30-05-1980
		AT 361895 B	10-04-1981
		AT 931377 A	15-09-1980
		AU 513160 B2	20-11-1980
		AU 3175977 A	28-06-1979
		BE 862371 A1	14-04-1978
		BR 7708690 A	15-08-1978
		CA 1108943 A1	15-09-1981
		CH 630269 A5	15-06-1982
		DE 2757528 A1	06-07-1978
		DK 584177 A	01-07-1978
		ES 465482 A1	16-09-1978
		FR 2375903 A1	28-07-1978
		GB 1542058 A	14-03-1979
		IT 1114947 B	03-02-1986
		JP 1258180 C	29-03-1985
		JP 53084881 A	26-07-1978
		JP 59035258 B	28-08-1984
		NL 7714610 A ,B,	04-07-1978
		NO 774457 A ,B,	03-07-1978
		NZ 185773 A	19-06-1979
		SE 414583 B	11-08-1980
		SE 7714554 A	01-07-1978
		SU 965341 A3	07-10-1982
		ZA 7707103 A	27-09-1978
EP 0364922 A	25-04-1990	JP 2111428 A	24-04-1990
		JP 2675594 B2	12-11-1997
		JP 2303532 A	17-12-1990
		JP 2675618 B2	12-11-1997
		JP 2303533 A	17-12-1990
		JP 2865311 B2	08-03-1999
		JP 2187387 A	23-07-1990
		JP 2825526 B2	18-11-1998
		AU 609644 B2	02-05-1991
		AU 4288689 A	19-07-1990
		DE 68902722 D1	08-10-1992
		DE 68902722 T2	18-03-1993
		EP 0364922 A1	25-04-1990
		US 5068067 A	26-11-1991
US 5043161 A	27-08-1991	NONE	